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SYNTHESIS OF CYCLOPROPYL ESTERS FROM SILYL ENOL ETHERS[1)]

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Cyclopropyl esters are conveniently prepared by direct addition of acid halides to the reaction mixture of Simmons-Smith reagent and silyl enol ethers. In this reaction, zinc iodide, a by-product of the Simmons-Smith reaction, operates as a Friedel-Crafts-type catalyst to activate acid halides.

There have been several methods for the synthesis of cyclopropyl esters, the fundamental derivative of cyclopropanols.[2)] However, these methods suffer from a lack of convenience or relatively low yields.

Now we wish to report a novel synthesis of cyclopropyl esters (2) from silyl enol ethers (1), Simmons-Smith reagent, and acid halides. It has been shown that the direct addition of acid halides to the reaction mixture of Simmons-Smith reagent and (1) gave good yields of (2). Typical experimental procedure for the synthesis of bicyclo[4.1.0]hept-1-yl acetate is as follows. To a stirred suspension of zinc-copper couple[3)] (0.16 mol) in anhydrous ether (110 ml) were added 1-trimethylsiloxycyclohexene (0.05 mol) and methylene iodide (0.08 mol) , and the mixture was refluxed for 21 hr. Then acetyl chloride (0.05 mol) was slowly added to the reaction mixture, which contained zinc iodide as well as the silyl cyclopropyl ether, and the mixture was refluxed for another 3 hr. After work-up the vacuum distillation of the ethereal solution gave bicyclo[4.1.0]hept-1-yl acetate in 65% yield: b.p. 89-90°C (30 mmHg), m/e 154 (M^+), i.r. (neat) 3050, 1750 cm^{-1}, p.m.r. δ 0.25-0.90 (m, 2H), 1.90 (s, 3H).[4)] The Table shows the results of the one-pot-synthesis of a variety of cyclopropyl esters from the corresponding silyl enol ethers.

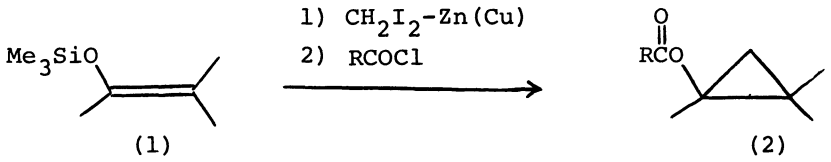

Table. Reaction of RCOCl with the reaction mixture of Simmons-Smith reagent and silyl enol ethers (1).

Entry	Enol Ethers (1)	Acid Halides	Yields of (2)[a]
1	1-Trimethylsiloxycyclohexene	CH_3COCl	65%
2		PhCOCl	43%[b]
3		PhCOCl[c]	70%
4		$CH_3CH=CHCOCl$	58%
5	1-Trimethylsiloxycyclopentene	CH_3COCl	70%
6	α-Trimethylsiloxystyrene	CH_3COCl	48%
7	1-Ethoxycyclohexene	CH_3COCl	—[d]

a) Isolated yields are given. b) The formation of ethyl benzoate due to the benzoylation of the solvent was observed. c) Two equivalents of benzoyl chloride were used. d) Cyclopropyl acetate was not formed, but 1-ethoxy-bicyclo[4.1.0]heptane which was the product of the Simmons-Smith reaction was obtained in 56% yield.

Zinc iodide, which is the by-product of Simmons-Smith reaction, seems to play an important role for the activation of acid halides in the present synthesis. Treatment of an isolated silyl cyclopropyl ether, 1-trimethylsiloxy-bicyclo[4.1.0]heptane, with acetyl chloride in ether at 38°C gave no cyclopropyl ester without the presence of zinc iodide.[5] It should be also noted that the formation of cyclopropyl esters was restricted to the case of siloxy compounds (see entry 7 in Table). This synthesis of cyclopropyl esters may be of value, especially for the bicyclic ones which are hardly accessible by previous methods.

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REFERENCES and NOTES

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4) Spectral and analytical data were entirely consistent with the structures of all new compounds.
5) There have been some reports on the formation of esters from alkoxysilanes and acid halides (in drastic reaction conditions and in poor yields)[ref.6)].
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